U.S. UTILITY PATENT APPLICATION

IN THE NAME OF

Michael GRAETZEL
Robert PLASS
Udo BACH

Filed: July 30, 2001

SOLID STATE HETEROJUNCTION AND SOLID STATE
SENSITIZED PHOTOVOLTAIC CELL

Claiming priority from European
Patent Application No. 00810681.7
Filed July 28, 2000

Express Mail Label No. EL210001200US

Date of Deposit July 30, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR §1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, DC 20231.

Sheryl X Hutchings

Signature of person mailing paper or fee

Attorney Docket No. 16090-23

Solid state heterojunction and Solid state sensitized photovoltaic cell

The present invention concerns a solid state p-n heterojunction, comprising an electon conductor and a hole conductor. The invention concerns also a solid state sensitized photovoltaic cell, in particular a solar cell.

The dye sensitized solar cells (DYSC), are more and more maturing into a technically and economically credible alternative to the conventional p-n junction photovoltaics. Photoelectrochemical (PEC) liquid junction cells based on the photosensitization of semiconductor TiO_2 layers with molecular sensitizers attracted renewed interest after Graetzel et al reported energy conversion efficiencies >10%, in Nature, 353 (1991) 737. In 1998, Graetzel et al reported in Nature, 395 (1998) 583, a more innovative all solid state cell based on a heterojunction sensitized by a molecular dye where an amorphous organic hole transport material replaced the liquid electrolyte.

The crucial part in these cells is the dye itself. Only a very limited number of dyes give high photocurrent quantum yields and are reasonably stable against photo-degradation. Some of the organic dyes exhibiting high light absorption are sensitive to air and water.

It is therefore a target of the present invention to propose photovoltaic cells having improved stability against photo-degradation and environmental influences. It is another target of the invention to achieve higher photocurrent quantum yields, higher photovoltages and hence higher conversion yields in the visible part of the light spectrum.

These aims are achieved by means of a solid state p-n heterojunction comprising a solid electron conductor, - i.e. a n type semiconductor, and a hole conductor, - i.e. a p-type semiconductor, further comprising a sensitising semiconductor, said sensitising semiconductor being located at the interface between the electron conductor and the hole conductor.

For the purpose of sensitization, the sensitizing semiconductor shall be light absorbing in the visible and the near infrared parts of the light spectrum, preferably up to 950 nanometers (eq to 1.4 eV).

The sensitizing semiconductor maybe provided in form of a coating film at the surface of the electron conductor. This coating film is not necessarily continuous. Only a part of the surface of the electron conductor, i.e. a part of the surfaces of the pores of a porous electron conductor may be covered by coating portions.

The sensitizing semiconductor may be provided in form of particles adsorbed at the surface of the electron conductor. The term "particles" herein refers to particles of various sizes, below a nanometer, in the nanometer range, or bigger, but excludes single discrete molecules.

A preferred kind of particles of sensitizing semiconductor for providing a solid state p-n heterojunction according to the present invention are quantum-dots.

Thereby, a preferred object of the present invention is a new embodiment of a sensitized solar cell where the molecular sensitizer is replaced by a small semiconductor particle, referred to in scientific papers as "nano-dot" or "quantum dot" or "Q-dot". Quantum dots are semiconductor particles of nanometer size wherein a gradual translation from solid state to molecular structure occurs as the particle size decreases. The quantum dots are adsorbed at the heterojunction constituted by a n-type semiconductor and a p-type semiconductor.

Preferably, the n-type semiconductor is a finely divided and sintered large band gap ceramic oxide. Various metal oxides like Ta_2O_5, Nb_2O_5, SnO_2, ZnO may be used as solid electronic conductors, whereas nanocrystalline TiO_2 (anatase) is preferred.

The hole conductor may be selected from hole transporting inorganic solids like copper iodide or copper thiocyanate. Typically, the hole conductor may be an organic charge transport material. This organic charge transport material may be a polymer, like poly-tiophen or poly-arylamin. The hole conductor of the present invention may also be an amorphous, reversibly oxidizable organic non-polymeric compound.

As such a compound, the hole conductor may be selected from the group consisting of spiro- and hetero spiro compounds of general formula (I)

$$K1 \quad \varphi \quad K2 \tag{I}$$
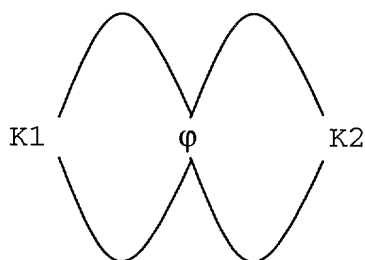
Wherein φ is one of C, Si, Ge or Sn, and K1 and K2 are, independently one of the other, conjugated systems. A particularly preferred hole conductor is 2,2',7,7'-tetrakis (N,N-di-p-methoxyphenyl-amine) 9,9'-spirobifluorene, herein further called OMeTAD.

As quantum dots, particles consisting of CdS, Bi_2S_3, Sb_2S_3, or Ag_2S may be used, whereas PbS is preferred. Other compounds suitable for making quantum-dots are In As, **InP**, CdTe, CdSe, HgTe. Solid solutions of HgTe and CdTe or of HgSe and CdSe are also suitable.

A preferred quantum dot sensitized nanocrystalline heterojunction is constituted of sintered particles of nanocrystalline TiO_2 onto which PbS particles in the nanometer range are adsorbed as sensitizers, the pores between the particles being filed with amorphous OMeTAD.

The mesoscopic nature of the heterojunction results in a high contact area of the junction, which is prerequisite for efficient solar light harvesting by the quantum dots. Light is absorbed by the Q-dots and produces electron-hole pairs. The electrons are injected from the Q-dots into the electron conducting solid while the holes are injected in the hole conducting side of the junction. In this way electric power is produced from light.

While the sensitization of oxide semiconductors by Q-dots has already been reported for liquid junction cells by Vogel et al, in Chem. Phys. Lett., 174 (1990) 241, these devices show notorious problems with corrosion and photo-corrosion of the Q-dots by the electrolyte, rendering them unsuitable for sensitization. The present invention realises a solid state heterojunction cell that does not present these disadvantages and hence can be used for the conversion of sunlight to electric power.

Quantum dot sensitized heterojunction cells offer several advantages. The band gaps and thereby the absorption ranges are adjustable through the particle size or by adjusting the relative concentrations of components in solid solutions like HgTe/CdTe or HgSe/CdSe. The band gap of these solutions may be adjusted to approach the optimal value for conversion of sunlight to electric power, which is about 1.4-1.5 eV.

Furthermore, compared to organic dyes, quantum dot sensitization offers improved stability, since the surface of the Q-dots can be modified to improve their photostability.

Another advantage is that the optical cross section of the Q-dots is significantly larger than the one of the molecular dyes. This allows to employ thinner films resulting in higher photovoltages as well as better fill factors of the cell, and hence higher conversion yields. Whereas only a limited number of molecular dyes suit the requirements of DYSC, Q-dot semiconductors have very high extinction coefficients and hence are very effective sensitizers. Since photo generated e^- and h^+ can be separated effectively as in n-p junctions, quantum dot sensitization offers a means to combine the mechanical features, efficiency and weather-ruggedness of single crystalline or polycrystalline p-n photovoltaics with an excellent spectral range coverage.

Other features and advantages of the present invention will appear to those skilled in the art from the following description of an embodiment of a solid state sensitized photovoltaic cell, from the description of a process for making a solid state heterojunction and from measurements made with such a cell, in conjunction with the drawings, among which:

- figure 1 shows a schematic view of a solid state sensitized photovoltaic cell;

- figure 2 is an enlarged view of a heterojunction within the nanocrystalline TiO_2 layer;

- figure 3 shows absorption spectra of TiO_2 plates with different deposition treatments; and

- figure 4 shows the photo current generation efficiency as a function of wavelength for Q-dot sensitized solid state heterojunction solar cells.

Figure 1 shows the schematic build up of a solid state sensitized photovoltaic cell. From bottom to top there are:

- an ITO transparent glass support 1;
- the glass support 1 is coated by a transparent conducting layer 2 made of F doped SnO_2, thereby the coated glass acts as a working electrode, which collects charge and current.
- a dense TiO_2 layer 3 for avoiding direct contact between the organic hole conductor and the SnO_2, which would short circuit the cell;
- a quantum dot sensitized nanocrystalline layer 4, forming a heterojunction, which is build up as will be explained bellow;
- the back contact 5 of the cell is made of a fine gold layer of 10 nanometers covered by a thick nickel layer for a better current collection.

   Figure 2 shows a magnified schematic view of the microscopic structure of the layered heterojunction: at the surface of TiO_2 particles 6, are adsorbed Q-dots 7; the spaces are filled with particles 8 of an organic hole conductor.

Example: process for making a layered heterojunction

   The compact TiO_2 layer is deposited on the SnO_2-coated glass by spray pyrolysis. This process is performed following the procedure described in the thesis No. 2187 at EPFL (Ecole Polytechnique Fédérale de Lausanne) of Udo Bach. The nanoporous TiO_2 layer is deposited by screen printing. The plates are thereafter sintered at a temperature of 450°C for 15 min. This results in a layer with a thickness of about 2 μm. The plates are thereafter stored in water free atmosphere.

   The technique used to deposit the Q-dots follows the procedure published by Weller et al in J. Phys. Chem. 98, 1994, 3183. Two solutions are needed for this technique, the first one is a saturated $Pb (NO_3)_2$ solution in water, and the second one a 0.3M Na_2S solution in water. The plates are immersed for 1 minute in the first solution. Thereafter, they are rinsed with water and dipped into the second solution for

about 10 sec and then rinsed again. This deposition procedure
may be repeated several times.

After the deposition of the Q-dots, the hole-conductor is
introduced into the pores of the nanocrystalline structure by
spin-coating. The spin-coating solution is a 30% by weight
solution of OMeTAD in chlorobenzene. The OMeTAD may be doped
with 0.2% of OMeTAD⁻. An amount of 15µl of spin-coating
solution is used for each plate. Subsequently, the solvent is
evaporated.

A semi-transparent gold back contact is evaporated on top of
the heterojnction layer under vacuum. A second contact layer
made of nickel is sprayed onto the first one.

Absorption spectra are measured with a Hewlett-Packard 8453
spectrometer and are shown in Figure 3. Figure 3 shows that
repeating the Q-dot deposition treatment results in an
increase of the visible absorption of the electrode. With each
deposition, the optical density increases and the electrode
becomes strongly coloured. The Q-dots are getting bigger with
each treatment.

Figure 4 shows the wavelength response of the photocurrent
produced by the device. The incident photon to current
conversion efficiency (IPCE) is plotted as a function of the
wavelength of the monochromatic light. The conversion yields
are high, exceeding 10 percent in the visible. This proves
that the sensitization of the heterojunction by the quantum
dots functions well.

From these measurements, it can be seen that there is an
optimum in the number of times the deposition treatment is
repeated. For this embodiment, if only one treatment is done,
there is not enough Q-dots formed on the TiO_2 surface. On the
other hand, if there are too many deposition treatments,
typically 10, as shown in figure 4, the Q-dots get too big and
the efficiency drops.